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ON AN EQUATION FOR THE VISCOSITY OF MIXTURES

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Received October 28, 1937

SUMMARY

An expression of the form $\log \eta_{sol} - \frac{1}{3} \log \rho_{sol} = C_1 + C_2 x_2$ can be deduced from Andrade's equation for viscosity on the basis of certain assumptions. The applicability of the above equation has been tested by considering 18 binary systems. On plotting the value of $\log \eta_{sol} - \frac{1}{3} \log \rho_{sol}$ against x_2 the graphs have been found to be straight lines in many cases. In the case of systems, the components of which have polar properties and are dissimilar in nature, the divergence is marked. This is explained as due to loose compound formation. The viscosity values calculated from MacLeod's equation have been compared with those obtained from the above equation. The latter equation gives somewhat better values.

Frequent attempts have been made to find a relationship between the viscosity of binary mixtures and their compositions. A linear formula based on the mixture law has often been tried but has been found inadequate. It was suggested that the divergence from the linear equation was due to the lack of the correct method of expressing the composition. According to Drucker and Kassel,[4] concentration should be expressed as weight percentages, whilst Kendall[7] considers it more logical to express the composition as molar concentrations. MacFarlane and Wright[9] have, however, shown that whatever method of plotting the experimental data be adopted, viscosity cannot be expressed as an additive property.

Findlay[5] considers that fluidity, which represents the inverse of viscosity, might be expressed more consistently by the mixture law formula. Bingham and

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Frequent attempts have been made to find a relationship between the viscosity of binary mixtures and their compositions. A linear formula based on the mixture law has often been tried but has been found inadequate. It was suggested that the divergence from the linear equation was due to the lack of the correct method of expressing the composition. According to Drucker and Kassel,[4] concentration should be expressed as weight percentages, whilst Kendall[7] considers it more logical to express the composition as molar concentrations. MacFarlane and Wright[9] have, however, shown that whatever method of plotting the experimental data be adopted, viscosity cannot be expressed as an additive property.

Findlay[5] considers that fluidity, which represents the inverse of viscosity, might be expressed more consistently by the mixture law formula. Bingham and

MacMaster[3] attempted to express fluidities by an additive formula but found it inadequate.

Attempts have also been made to express viscosity by means of a logarithmic formula. The equation proposed by Arrhenius[2] gave divergent values in concentrated solutions. Kendall modified the Arrhenius formula in which he used molar percentages in place of volume percentages. Later Kendall and Monroe[8] proposed the equation

$$\log \eta_{sol} = x_1 \log \eta_1 + x_2 \log \eta_2$$

where x_1 and x_2 represented the molar percentages of the two components. Both these equations were subsequently found by them as unsatisfactory.

In a previous paper[6] we have found that the logarithms of the relative viscosities of solutions when plotted against the molar fraction of the solute generally gave straight lines up to 50% mixtures. At higher concentrations the plot was still a straight line but with a different slope. For dilute solutions the formula $\log \eta/_{\eta_1} = C_1\, x_2 + C_2$, where C_1 and C_2 were constants, was fairly satisfactory.

Kendall[7] has classified binary mixtures into two groups, the ideal and the non-ideal solutions. A binary system was considered ideal when on mixing the components there was no volume change and no heat evolution. Ideal solutions, however, are hardly attained in practice and even the systems which have been considered by Kendall as ideal show distinct variations in density on mixing. It is evident, therefore, that an allowance has to be made for the change in volume that sets in when the mixture is made. In the following pages an equation involving the necessary density correction has been derived from Andrade's viscosity equation on the basis of certain assumptions.

According to Andrade[1] the viscosity of a pure liquid is given by $\eta v^{\frac{1}{3}} = A.\, e^{c/vT}$ where v is the specific volume, T the absolute temperature and A and C are constants. For a particular temperature the equation can be written as $\eta/\rho^{\frac{1}{3}} = A.\, e^{\beta\rho}$ where $\beta = \frac{C}{T}$.

If we assume, as has been done by Spells,[11] that Andrade's equation can be applied to the case of solutions also, the viscosity of a solution will be expressed by the equation $\eta/\rho^{\frac{1}{3}} = A_1.\ e^{B\rho}$ where A_1 and B are constants. Expressing in logarithmic form we get

$$\log \eta_{sol} - \tfrac{1}{3} \log \rho_{sol} = C_1 + B\rho_{sol},$$

where C_1 and B are constants.

The variation of the constant B with concentration has been considered by Spells, who has concluded that the constant is a function of the composition of the mixture. If we assume that $B\rho_{sol}$ is directly proportional to x_2, where x_2 represents the molar fraction of the solute, the above equation reduces to the form

$$\log \eta_{sol} - \tfrac{1}{3} \log \rho_{sol} = C_1 + C_2\, x_2 .$$

We have tried to apply the above equation to a number of binary systems and we have found the plot of $\log \eta_{sol} - \frac{1}{3} \log \rho_{sol}$ against x_2 to be generally a straight line. For convenience of plotting the values for the relative viscosities and relative densities have been used. The following eighteen systems have been analysed :—

(1) Phenetole-diphenyl ether, (2) ethyl benzoate-benzyl benzoate, (3) ethyl acetate-ethyl benzoate, (4) phenetole-diethyl ether, (5) diethyl ether-diphenyl ether, (6) ethyl acetate-benzyl benzoate, (7) benzene-ethyl benzoate, (8) toluene-ethyl benzoate, (9) toluene-benzyl benzoate, (10) benzene-benzyl benzoate, (11) ethylene dichloride-ethylene dibromide, (12) trichloracetic acid-acetone, (13) acetic acid-acetone, (14) phenol-benzene, (15) phenol-acetone, (16) trichloracetic acid-acetic acid, (17) acetic acid-ethyl benzoate, (18) acetic acid-ethyl acetate.

The first ten of the above-named systems have been analysed by Kendall and co-workers, whilst the system ethylene dichloride-ethylene dibromide has been investigated by MacFarlane and Wright. In every case these authors have found all previously proposed equations to be inadequate. On plotting $\log \eta_{sol} - \frac{1}{3} \log \rho_{sol}$ against x_2 we have found the graphs in the majority of cases to be very nearly straight lines. Thus the logarithmic equation represents the experimental values fairly satisfactorily. The graphs are given in figures 1 to 3 and the viscosity values are given in tables 1 to 18.

An expression for the viscosity of binary systems has been deduced by MacLeod[10] on the basis of the change of free space on mixing. He used the equation $\eta_{sol} = \eta_1^{m_1} \frac{x_1}{x} + \eta_2^{m_2} \frac{x_2}{x}$ where m_1 and m_2 are the molar fraction of the components and x_1, x_2, x are the amounts of free space of the two components and of the mixture respectively. Some of the systems analysed in the present paper have also been studied by MacLeod. It was, therefore, considered interesting to compare MacLeod's values with those obtained with the logarithmic equation. In the last three columns of tables 1 to 6 are given the percentage deviations obtained on the basis of MacLeod's equation and those calculated from the present equation. As will be seen from these tables, except in the case of the system ethyl acetate-benzyl benzoate, the logarithmic equation gives somewhat better values.

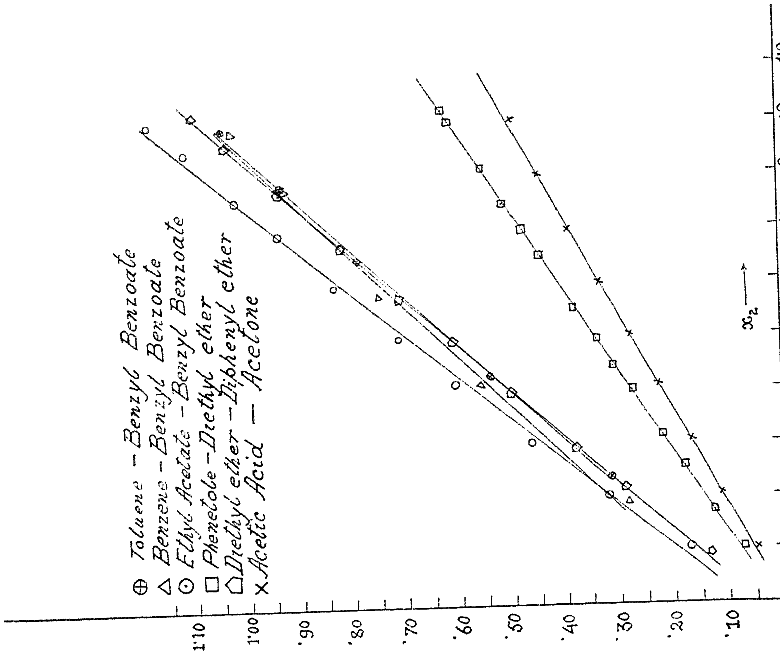
Toluene - Benzyl Benzoate
Benzene - Benzyl Benzoate
Ethyl Acetate - Benzyl Benzoate
Phenetole - Diethyl ether
Diethyl ether - Diphenyl ether
Acetic Acid — Acetone
1.10
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
x_2 →

Fig. 2

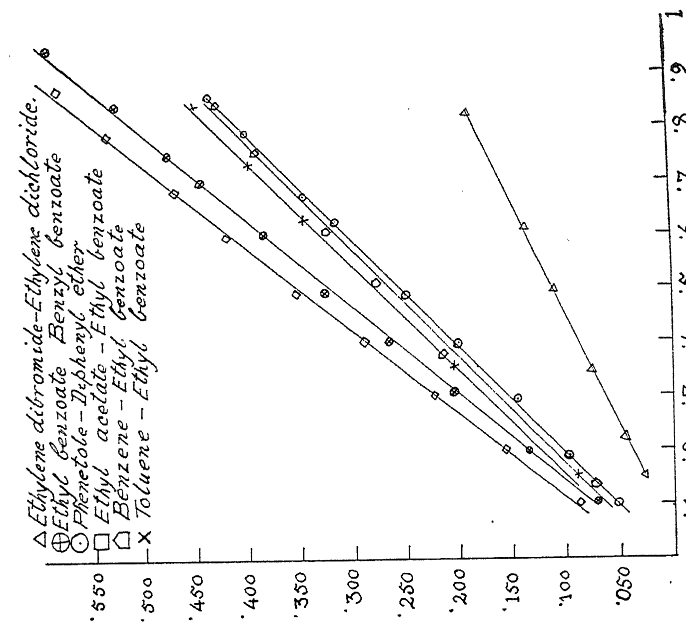
Ethylene dibromide-Ethylene dichloride.
Ethyl benzoate Benzyl benzoate
Phenetole - Diphenyl ether
Ethyl acetate - Ethyl benzoate
Benzene - Ethyl benzoate
Toluene - Ethyl benzoate
.550
.500
.450
.400
.350
.300
.250
.200
.150
.100
.050
.1
.2
.3
.4
.5
.6
.7
.8
.9
1

Fig. 1

From an examination of the graphs (fig. 3) it will be seen that in the case of the systems phenol-benzene, trichloracetic acid-acetone, phenol-acetone, trichlor-

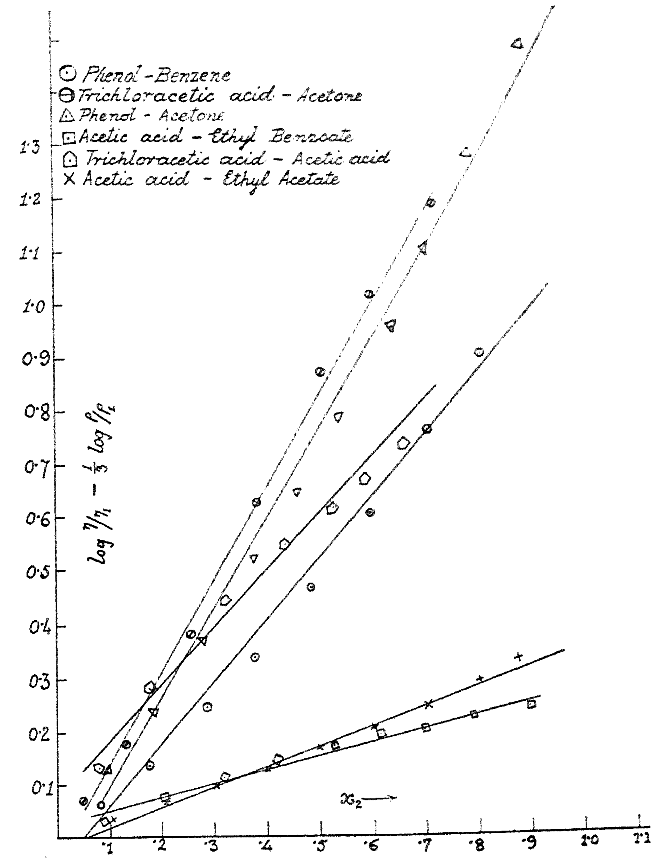

Fig. 3

acetic acid-acetic acid, acetic acid-ethyl benzoate, and acetic acid-ethyl acetate the agreement is not so satisfactory as in the case of the remaining systems. The order of the deviations is too large to be due to any experimental error. In the case of these systems, however, one or both of the components have Polar properties and the nature of the components are dissimilar. There is thus a pronounced possibility of the formation of loose compounds. It will be reasonable to assume that in these cases the divergences are due to a form of loose chemical combination. The system phenol-benzene has also been studied by MacLeod. As will be seen from table 14, the divergences from both MacLeod's equation and the present equation are of the same order.

Thus the logarithmic equation is applicable to a large number of the systems named above. It would appear, therefore, that Andrade's viscosity equation applies fairly well to the case of binary solutions also. In applying the equation $\log \eta_{sol} - \frac{1}{3} \log \rho_{sol} = C_1 + C_2 x_2$ it has been assumed that the constant A of Andrade's equation does not vary much with changes of concentration. That the above assumption is at least approximately true is borne out by the fact that in the case of a large number of the systems viscosity values are in accordance with the above equation.

In conclusion it might be stated that an expression similar to Andrade's equation has been deduced by MacLeod from his own equation.

One of us is indebted to the Patna University for a research scholarship which has enabled him to carry on the work.

Table I

Phenetole-Diphenyl Ether

Mol fraction ether	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	0·9618	·01158	...	...	...	...	...
·0994	0·9755	·01309	·05120	·01309	0·0	·01328	+1·5
·1873	0·9870	·01451	·09425	·01451	0·0	·01479	+1·5
·2963	0·9993	·01632	·14356	·01645	+0·8	·01672	+2·4
·3998	1·0111	·01862	·19907	·01874	+0·6	·01883	+2·1
·4895	1·0206	·02096	·24921	·02088	−0·4	·02092	−0·2
·6269	1·0346	·02455	·31583	·02458	+0·1	·02450	−0·2
·6747	1·0396	·02630	·34503	·02612	−0·7	·02610	−0·7
·7928	1·0510	·03003	·40106	·03003	0·0	·02960	+0·3
·8633	1·0573	·03264	·43641	·03264	0·0	·03230	+0·4

Table II

Ethyl Benzoate—Benzyl Benzoate

Mol fraction ethyl-benzoate	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	1·0431	·02014	...	...	...	...	...
·1037	1·0524	·02371	·06962	·02395	+1·0	·02381	+0·4
·1977	1·0603	·02749	·13276	·02749	0·0	·02755	+0·2
·3094	1·0683	·03249	·20426	·03232	−0·5	·03245	−0·1
·4059	1·0760	·03740	·26433	·03740	0·0	·03739	0·0
·4946	1·0825	·04309	·32596	·04236	−1·8	·04265	−1·0
·6055	1·0910	·04948	·38388	·04948	0·0	·05110	+3·1
·7027	1·0967	·05695	·44418	·05695	0·0	·05930	+3·3
·7525	1·1005	·06108	·47411	·06108	0·0	·06340	+3·6
·8451	1·1053	·06898	·52631	·06995	+1·4	·07100	+2·9
·9535	1·1104	·08039	·59212	·08129	+1·1	·08280	+3·0

Table III

Ethyl Acetate-Ethyl Benzoate

Mol fraction ethyl-benzoate	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	0·8948	·004239	...	...	...	...	...
·1008	0·9204	·005188	·08366	·005263	+1·4	·005240	+1·0
·2023	0·9440	·006178	·15585	·006188	+0·2	·006455	+4·2
·3011	0·9598	·007247	·22275	·007235	−0·1	·007470	+3·0
·4002	0·9740	·008478	·28875	·008406	−0·85	·008590	+1·1
·4956	0·9866	·009851	·35208	·009748	−1·20	·009760	−1·0
·6027	0·9992	·01157	·42005	·01149	−0·7	·01140	−1·4
·6869	1·0101	·01292	·46647	·01292	0·0	·01280	−0·7
·7912	1·0223	·01514	·53358	·01529	+1·0	·01492	−1·6
·8784	1·0320	·01704	·58355	·01739	+1·5	·01708	−0·2

Table IV

Phenetole-Diethyl Ether

Mol fraction phenetole	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	·7139	·002233	...	...	...	...	...
·0996	·7458	·002674	·07196	·002692	+0·7	·002722	+1·9
·1697	·7656	·003057	·12630	·003050	−0·2	·003094	+1·2
·2515	·7891	·003494	·17995	·003478	−0·5	·003560	+2·1
·3118	·8059	·003866	·22084	·003841	−0·6	·003960	+2·5
·3952	·8282	·004406	·27366	·004406	0·0	·004497	+2·1
·4421	·8387	·004809	·30985	·004749	−1·2	·004840	+0·7
·4894	·8488	·005154	·33821	·005154	0·0	·005141	−0·1
·5499	·8628	·005713	·38057	·005674	−0·7	·005586	−2·2
·6484	·8853	·006667	·44390	·006660	−0·1	·006527	−2·0
·6974	·8970	·007152	·47250	·007162	+0·1	·007054	−1·4
·7477	·9083	·007856	·51146	·007812	−0·6	·007800	−0·9
·8145	·9230	·008671	·55200	·008665	−0·1	·008511	−1·9
·9025	·9427	·009993	·61058	·009993	0·0	·009926	−0·8
·9255	·9471	·01027	·62177	·01039	+1·1	·01027	0·0

Table V

Diethyl Ether-Diphenyl Ether

Mol fraction phenyl ether	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	0·7139	·002233	...	...	...	...	...
·0908	0·7601	·003106	·13353	·003183	+2·5	·003061	−1·5
·2174	0·8213	·004552	·28901	·004552	0·0	·004523	−0·5
·2912	0·8554	·005733	·38032	·005639	−1·6	·005738	+0·1
·3924	0·8974	·007614	·49959	·007603	−0·2	·007735	+0·7
·4898	0·9311	·009926	·60945	·009827	−1·0	·009935	+0·1
·5755	0·9583	·01258	·70813	·01246	−0·9	·01227	−2·5
·6703	0·9862	·01631	·81682	·01614	−1·0	·01570	−3·8
·7807	1·0181	·02153	·93283	·02153	0·0	·02110	−2·0
·8682	1·0387	·02737	1·03411	·02741	+1·5	·02655	−3·0
·9296	1·0542	·03158	1·09406	·03251	+2·9	·03153	−0·2

Table VI

Ethyl Acetate-Benzyl Benzoate

Mol fraction Benzyl-benzoate	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$	η_{cal}	% age deviation	η from MacLeod equation	% age deviation
·0000	0·8948	·004239	...	...	...	..	...
·1020	0·9394	·006406	·17228	·006672	+4·1	·006453	+0·9
·2010	0·9720	·009116	·32056	·009000	−1·3	·008705	−0·5
·3027	0·9988	·01275	·46232	·01211	−5·0	·01240	−2·5
·4137	1·0247	·01789	·60574	·01706	−4·7	·01740	−3·0
·5000	1·0454	·02299	·71179	·02197	−4·1	·02293	−0·1
·5999	1·0625	·03047	·83175	·02966	−2·6	·03021	−0·9
·6998	1·0778	·03881	·93475	·03927	+1·2	·04010	+3·0
·7653	1·0867	·04711	1·01772	·04711	+0·0	·04750	+0·9
·8574	1·0975	·05938	1·11679	·06140	+3·4	·05934	−0·1
·9124	1·1048	·07003	1·18753	·07413	+5·5	·07180	+2·5

Table VII

Benzene-Ethyl Benzoate

Mol fraction ester	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$
·0000	0·87309	·006051	...
·1302	0·90592	·007244	·07280
·3808	0·95700	·01018	·21258
·5128	0·98109	·01200	·27662
·6111	0·99387	·01327	·32227
·7598	1·01459	·01557	·38870
·8479	1·02350	·01709	·42787

Table VIII

Toluene-Ethyl Benzoate

Mol fraction ester	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$
·0000	0·86244	·005520	...
·1524	0·89770	·006845	·08764
·3546	0·93921	·009076	·20360
·6299	0·98844	·01279	·34519
·7349	1·00530	·01452	·39782
·8442	1·03160	·01655	·45092

Table IX

Toluene-Benzyl Benzoate

Mol fraction ester	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	0·86244	·005520	...
·2367	0·95282	·01183	0·31662
·4261	1·0069	·02015	0·53990
·6502	1·0584	·03614	0·78658
·7890	1·0829	·05080	0·93096
·9002	1·0966	·06660	1·04664

Table X

Benzene-Benzyl Benzoate

Mol fraction ester	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	0·87309	·006044	...
·1886	0·95327	·01196	0·28372
·4124	1·0175	·02301	0·55843
·5832	1·0544	·03584	0·74471
·7827	1·0831	·05478	0·92609
·8952	1·1061	·06883	1·02220

Table XI

Ethylene Dichloride-Ethylene Dibromide

Mol fraction dibromide	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	1·238	·007812	...
·1499	1·389	·008648	·02755
·2209	1·456	·009179	·04657
·3450	1·577	·01006	·07475
·4941	1·715	·01117	·10809
·6125	1·826	·01216	·13591
·8250	2·016	·01421	·19010

Table XII

Trichloracetic acid-Acetone

Mol fraction acid	ρ_{obs}	η_{obs}	$\log \eta/_{\eta_1} - \frac{1}{3} \log \rho/_{\rho_1}$
·0000	0·7872	·003065	...
·0484	0·8541	·003680	0·06773
·1316	0·9342	·004855	0·17163
·2543	1·0730	·008156	0·38029
·3826	1·2090	·01433	0·62319
·5048	1·3190	·02571	0·86764
·5971	1·4000	·03829	1·01363
·7175	1·4830	·05808	1·18640

Table XIII

Acetic acid-Acetone

Mol fraction acid	ρ_{obs}	η_{obs}	$\log \eta/_{\eta_1} - \frac{1}{3} \log \rho/_{\rho_1}$
·0000	0·7872	·003065	...
·0996	0·8089	·003496	·04731
·2035	0·8351	·004046	·11219
·3025	0·8568	·004636	·16751
·4049	0·8847	·005350	·22513
·4986	0·9064	·006098	·27837
·5973	0·9333	·006994	·33363
·6968	0·9609	·008026	·38920
·8015	0·9907	·009213	·44489
·9037	1·0255	·01036	·49081

Table XIV

Phenol-Benzene

Mol fraction phenol	ρ_{obs}	η_{obs}	$\log \eta/_{\eta_1} - \frac{1}{3} \log \rho/_{\rho_1}$	η_{cal}	% age deviation	η_{cal} from MacLeod Equation	% age deviation
·0000	0·8772	·00629	...				
·0506	0·8880	·00683	·03400				
·0803	0·8949	·00724	·05820				
·1720	0·9133	·00865	·13253				
·2845	0·9370	·01126	·24334	·01211	+7·5	·0123	+8·6
·37575	0·9549	·01401	·33550				
·4836	0·9766	·01911	·46492	·02108	+10·3	·0196	+2·6
·5923	0·9976	·02642	·60466				
·7037	1·0194	·03811	·76061	·03771	−0·3	·0349	+8·4
·8043	1·0383	·05350	·90528				

Table XV

Phenol-Acetone

Mol fraction phenol	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	0·8031	·00360	...
·0922	0·8425	·00486	0·12336
·1830	0·8768	·00635	0·23368
·2750	0·9085	·00868	0·36445
·3760	0·9406	·01256	0·51995
·4580	0·9642	·01688	0·64495
·5360	0·9851	·02358	0·78679
·6340	1·0090	·03670	0·95535
·6980	1·0237	·04950	1·10324
·7830	1·0420	·07480	1·27988
·8890	1·0623	·11930	1·47998

Table XVI

Trichloracetic acid-Acetic acid

Mol fraction trichloracetic acid	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	1·049	·01121	...
·0737	1·129	·01532	·12483
·1777	1·223	·02228	·27592
·3209	1·337	·03362	·44191
·4348	1·409	·04346	·54595
·5262	1·457	·05176	·61682
·5853	1·491	·05859	·66752
·6581	1·508	·06854	·73383

Table XVII

Acetic acid-Ethyl Benzoate

Mol fraction ester	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3}\log \rho/\rho_1$
·0000	1·050	·01121	...
·0868	1·049	·01202	·03036
·2044	1·049	·01322	·07196
·3174	1·048	·01446	·11051
·4178	1·048	·01538	·13771
·5250	1·047	·01651	·16829
·6118	1·047	·01727	·18808
·6955	1·047	·01797	·19871
·7871	1·046	·01874	·22336
·8959	1·046	·01948	·24078

Table XVIII

Acetic acid-Ethyl Acetate

Mol fraction acid	ρ_{obs}	η_{obs}	$\log \eta/\eta_1 - \frac{1}{3} \log \rho/\rho_1$
·0000	0·8948	·004236	...
·1049	0·9092	·004590	·03234
·2070	0·9211	·004949	·06337
·3037	0·9308	·005331	·09396
·3990	0·9417	·005762	·12621
·4985	0·9557	·006289	·16224
·5996	0·9697	·006890	·19962
·6988	0·9850	·007668	·24376
·8011	1·0015	·008590	·29067
·8742	1·0165	·009430	·32915

References

1. Andrade (1934) *Phil. Mag.*, **17**, 497.
2. Arrhenius (1887) *Zeit. Phys. Chem.*, **1**, 285.
3. Bingham and MacMaster (1906) *Zeit. Phys. Chem.*, **57**, 234.
4. Drucker und Kassel (1911) *Zeit. Phys. Chem.*, **76**, 367.
5. Findlay (1909) *Zeit. Phys. Chem.*, **69**, 203.
6. Ganguly, P. B. and Chakrabertty, S. K. (1937) *Zeit. Anorg. Chem.*, **231**, 304.
7. Kendall, (1913) *Meddelnden K. Vetens. Nobel Inst.*, **25**, 2.
8. Kendall and Monroe (1917) *Jour. Amer. Chem. Soc.*, **39**, 1787.
9. MacFarlane and Wright, (1933) *Jour. Chem. Soc.*, 114.
10. MacLeod (1924) *Trans. Faraday Soc.*, **20**, 348.
11. Spells (1936) *Trans. Faraday Soc.*, **32**, 1936.

ACTION OF PARA-TOLUENE-SULPHONYL CHLORIDE ON PHENOLS CONTAINING AZO GROUPS

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SUMMARY

1. The action of para-toluene-sulphonyl chloride on some phenols containing azo groups has been studied. In each case an ester has been obtained in the presence of diethylaniline as the condensing reagent.

2. Monoazo and disazo phenols yield esters easily. Trisazophenol does not form an ester. In no case is the OH group replaced by Cl atom.

3. The reactivity of these esters with aniline has also been studied and it has been found that the esters are reactive only when at least one (NO_2) group is present in the ortho position nearest to the OH group, and another NO_2 or CH_3 group in the second benzene ring.

In 1908 Ullmann and Nadai[6-8] observed that para-toluene-sulphonyl chloride reacts with 2:4-dinitro-phenol in two ways. In presence of sodium carbonate as condensing reagent, it forms a para-toluene-sulphonyl ester, but if diethylaniline is used as a condensing reagent, the -OH group is replaced by chlorine atom and 1 : 2 : 4-chloro-dinitro-benzene is obtained. Mono-nitro-phenols, however, yield esters in presence of sodium carbonate as well as diethylaniline. This reaction was studied by Ullmann and his collaborators[9] and later more extensively by Sane and Joshi,[1-3] who investigated the influence of the various groups *viz.*, -CH_3, Cl, Br, I, -NO_2 etc., on the replaceability of the -OH group in this reaction.

The chloro derivatives which are formed by this reaction contain an active chlorine atom.[4,5] The para-toluene-sulphonyl esters of dinitrophenols which yield chloro-dinitro-benzenes in presence of diethyl aniline are also reactive and when heated with aniline react as follows:—

$$\underset{2:4}{(NO_2)_2}.\ C_6H_3.\ \underset{1}{O}.SO_2.\ C_6H_4.\ CH_3 + NH_2.\ C_6H_5 = (NO_2)_2.\ C_6H_3.\ NH.\ C_6H_5 + CH_3.\ C_6H_4.\ HSO_3.$$

All para-toluene-sulphonyl esters of phenols do not react in the above manner, and this reactivity is found to depend upon the groups which are present in the phenols.

In the following paper the influence of diazo groups alone or along with NO_2 and Br groups has been examined. Mono and disazo-phenols form ester easily but the -OH group is not replaced by chlorine atom, when diethylaniline is used as a condensing reagent. Symmetrical trisazophenol does not form an ester. The esters formed are, however, reactive, *i.e.*, react with aniline in the manner shown above, only when at least one NO_2 (acid) group is present, in the ortho position nearest to the -OH group; but one NO_2 is not sufficient by itself thus :—

$$C_6H_5.N:N.C_6H_2.\underset{6}{NO_2}.\underset{2}{Br}\,\underset{1}{OSO_2}.C_6H_4.CH_3$$

does not react with aniline but when NO_2 or CH_3 group is introduced into the second benzene ring the ester becomes reactive, thus :—

1. $$\underset{4}{NO_2}.C_6H_6.\underset{1\;1'}{N:N}.C_6H_3.\underset{3'}{NO_2}.\underset{4'}{O}.SO_2.C_6H_4.CH_3+NH_2.C_6H_5=$$
$$CH_3.C_6H_4.HSO_3+\underset{4}{NO_2}.C_6H_4.\underset{1\;1'}{N:N}.C_6H_3.\underset{3'}{NO_2}.\underset{4'}{NH}.C_6H_5$$

2. $$\underset{4}{CH_3}.C_6H_4.\underset{1\;1'}{N:N}.C_6H_3.\underset{3'}{NO_2}.\underset{4'}{O}.SO_2.C_6H_4.CH_3+NN_2.C_6H_5=$$
$$CH_3.C_6H_4.HSO_3+\underset{4}{CH_3}.C_6H_4\,\underset{1\;1'}{N:N}.C_6H_3.\underset{3'}{NO_2}.\underset{4'}{NH}.C_6H_5$$

EXPERIMENTAL

The toluene-sulphonyl esters of the azo-nitrophenols were obtained by heating calculated quantities of the respective azo-nitrophenols, paratoluene-sulphonyl-chloride and diethylaniline on a water-bath for 4 hours. The mixture was cooled and then treated with dilute HCl, in order to decompose the unchanged diethylaniline. The aqueous liquid was then decanted off and the residue shaken with a little alcohol when in most cases the solid ester separated out. This was filtered and recrystallised from a suitable solvent. The solvent commonly used was glacial acetic acid and in some cases toluene.

The reactivity of the above esters with aniline was also studied separately in each case, and it was observed that esters were reactive, only when at least one NO_2 group is present in the ortho position nearest to the OH group, and another NO_2 or CH_3 group in the second benzene ring—yielding substituted diphenylamine compounds.

For the preparation of the diphenylamine compounds, calculated quantities of the toluene-sulphonyl-esters of the azo-nitrophenol, freshly distilled aniline, ethyl alcohol and fused anhydrous sodium acetate were refluxed for an hour over a water-bath. The alcohol was then distilled off and the excess of aniline removed by HCl. The solid mass, which separated out was thoroughly washed with water and finally recrystallised from acetic acid or toluene. The compounds obtained are generally deeply coloured, either deep red, orange or yellow.

Table I

	Formulæ	Melting point	Yield	Sulphur found	Sulphur calculated	Reactivity with aniline	M.P. of the anilide	% Nitrogen found	% Nitrogen calculated
1	$C_6H_5.N:N.C_6H_3.NO_2.X$ ... 1 3 4	112°C	3·0 gm.	7·7%	8·0%	Not reactive	...	...	...
2	$C_6H_5.N:N.C_6H_2.NO_2.Br\ X$ 1 3 5 4	150°C	2·0	6·7%	6·7%	„	...	...	...
3	$NO_2.C_6H_4.N:N.C_6H_4.X$ ... 4′ 1′ 1 4	167°C	3·0	7·9%	8·0%	„	...	...	...
4	$NO_2.C_6H_4.N:N.C_6H_3.NO_2.X$ 4′ 1′ 1 3 4	157°C	3·4	7·28%	7·2%	Reactive	205 C	19·0%	19·2%
5	$NO_2.C_6H_4.N:N.C_6H_2(Br)_2.X$ 4′ 1′ 1 3:5 4	171°C	3·5	5·4%	5·88%	„	196 C	...	...
6	$NO_2.C_6H_4.N:N.C_6H_3.NO_2.X$ 3′ 1′ 1 3 4	148°C	2·5	7·1%	7·2%	„	180 C	18·9%	19·2%
7	$NO_2.C_6H_4.N:N.C_6H_4.X.$ ... 2′ 1′ 1 4	132°C	2·6	7·9%	8·0%	Not reactive	...	...	...
8	$NO_2.C_6H_4.N:N.C_6H_3.NO_2.X$ 2′ 1′ 1 3 4	154°C	2·0	7·16%	7·2%	Reactive	166 C	19·0%	19·2%
9	$(NO_2)_2.C_6H_3.N:N.C_6H_4.X$ ... 2′:4′ 1′ 1 4	125°C	2·0	7·4%	7·2%	Not reactive	...	...	...
10	$CH_3.C_6H_4.N:N.C_6H_3.NO_2.X$ 4′ 1′ 1 3 4	135°C	3·7	7·6%	7·78%	Reactive	138 C	17·0%	16·9%
11	$CH_3.C_6H_4.N:N.C_6H_3.NO_2.X$ 3′ 1′ 1 3 4	124°C	2·3	7·48%	7·78%	„	120 C	17·16%	16·9%
12	$CH_3.C_6H_4.N:N.C_6H_3.NO_2.X$ 2′ 1′ 1 3 4	134°C	3·4	7·6%	7·78%	„	146 C	17·2%	16·9%
13	$NO_2.C_6H_4.N:N.C_6H_3.CH_3.X$ 4′ 1′ 1 3 4	180°C	1·2	7·6%	7·78%	Not reactive	...	...	...
14	$(Br)_3.C_6H_2.N:N.C_6H_3.NO_2.X$ 2′:4′:6′ 1′ 1 3 4	163°C	4·0	4·9%	5·0%	Reactive	154 C	10·0%	10·01%
15	$(NO_2).C_6H_4.N:N.C_6H_3.Cl.X$ 4′ 1′ 1 3 4	178°C	2·7	7·4%	7·31%	Not reactive	...	...	...
16	$NO_2.C_6H_4.N:N.C_6H_3\ Br.X$... 4′ 1′ 1 3 4	178°C	2·4	6·6%	5·8%	„	...	...	...
17	$(C_6H_5\ N:N)_2.C_6H_3.X$ ... 2:4 1	152°C	1·6	7·0%	7·0%	„	...	...	...

* $X = O.SO_2C_6H_4\ CH_3$

The action of α-naphthylamine was also studied on one ester. In this case 2 gms. of the ester ($NO_2 C_6H_4 . N : N . C_6H_3 . NO_2 . O.SO_2 . C_6H_4 . CH_3$) was dissolved in about 40 c.c. boiling amyl alcohol, and then about 2 gms. of α-naphthylamine and 2 gms. of fused sodium acetate added. This was then heated for an hour under a reflux condenser. On cooling a solid mass separated out which was filtered and then treated with HCl and hot water in order to remove the unchanged α-naphthylamine, the residue was then recrystallised from toluene.

The table on page 220 summarises the experimental results of the present investigation.

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References

1. Sane, Chakravarti and Pramanick (1932), *Jour. Ind. Chem. Soc.*, 55–57.
2. Sane and Joshi (1924), *Jour. Chem. Soc.*, 2481–84.
3. Sane and Joshi (1932), *Jour. Ind. Chem. Soc.*, 59–65.
4. Sane and Joshi (1933), *Jour. Ind. Chem. Soc.*, 459.
5. Sane and Joshi (1933), *Jour. Chem. Soc.*, 313.
6. Ullman and Bruck, W. (1908) *Ber.*, **41**, 3932–39.
7. Ullman and Nadai (1908), *Ber.*, **41**, 1870–78.
8. Ullman and others (1909), *Annalen*, **366**, 79–118.
9. Ullman and Sane (1911), *Ber.*, **44**, 3730–37.

IONISATION OF F-REGION BEFORE SUNRISE

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SUMMARY

Curves have been drawn for the time of sunrise and sunset at different heights for Allahabad for the whole year and with the help of these curves, the height where the sun's rays are falling at the time of minimum ionisation of the F-region just before sunrise is found. Similar calculations have been made for Washington and Slough and from these it has been shown that this height is greater in winter and smaller in summer for all the latitudes. For higher latitudes (*e.g.*, Slough) the ionization always begins to rise after sunrise in the F-region while for lower latitudes (*e.g.*, Washington and Allahabad) we can roughly say that the ionization begins to rise before sunrise in winter and after sunrise in summer.

It is now well recognised that the ionisation of the upper atmosphere is due to the action of the ultra-violet rays of the sun on the molecules of N_2 and O_2. The correctness of the solar origin of ionisation has been established in the eclipse expeditions of 1932 in the case of the E and F_1-layers, but in the case of F_2-layer, the observations have not yet yielded any decisive result. The F_2 layer has been found to behave in an anomalous way in other respects as well. Pederson[7] showed on the basis of the solar origin of ionisation that in the daytime the maximum concentration of electrons should vary as $\text{Cos}^{\frac{1}{4}}\psi$ (where ψ=zenith distance of the sun), but this law is apparently verified only in the case of the E and F_1-layers and not in F_2-layer. The F-layer[2] in the Ionisphere breaks up into two regions F_1 and F_2 during the day when the sun is fairly high and its angular zenith distance is less than about 40°. These two layers coalesce later, toward night fall and we have only one region which is usually supposed to be a continuation of the F_2-region. The F_2-region is thus only a daylight phenomenon. The ionization in lower F_1-layer is always found to have a maximum value near about noon as we should expect if the ionization be due to solar radiation but it is not so with the F_2-region. The daytime ionization in the F_2-region is found to have two maxima in the summer, one a few hours before noon and the other late in the afternoon.[5] The ionisation in the F_2-layer during the night is found to have one minimum during the summer and two minima in the winter, and there occurs a maximum at about 1 A.M. To explain these anomalous behaviours of the F_2-region, Appleton[1] thinks that during daytime in summer the F_2-layer heights are heated to about 1200° K by sunlight and then the ionised layers expand and concentration falls. So there is a minimum at

noon. The very hypothesis of a higher temperature on a summer morning than on a winter morning also explains the anomaly of two minima in the winter and one minimum in summer at night as a reduced ion production due to the reduced air density at the level of maximum ion production. But Berkner[3] contended that if this explanation were correct then in the southern hemisphere, as the seasons are reversed the conditions in the layer ought to be reversed, but his observations showed that this was not the case. The variation of the maximum density curve was found to be the same in both the hemispheres at the same instant throughout the year. It appears, therefore, that the F_2-region ionisation is a complex phenomenon. A minimum of ionisation in the region has however been always observed sometime before sunrise. The present investigation was undertaken to see whether the increase in ionisation begins to take place when the sun rises in the F_2-region.

Sunrise and Sunset in the Upper Regions

For this we require a formula to calculate the time of sunrise and sunset at different heights for different seasons. The height 'h' at which the sun rises when the time is 't'' is given by

$$h = 6480\,(\sec\eta - 1) \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

where $\sin\eta = -(\cos t' + \tan\delta\tan\varphi)\cos\delta\cos\varphi \qquad \ldots \qquad \ldots \qquad (2)$

t' = time between the time of sunrise at height 'h' and midday. (This will give us apparent time. To convert it into mean solar time, the equation of time is to be added.)

η = The angle by which the sun is below the horizon at the time t'

φ = Latitude of the place

δ = Declination of the sun.

The calculations for the time of sunrise and sunset at different heights over Allahabad were made with the aid of formulæ (1) and (2) for the whole year at intervals of fifteen days and these are represented in figs. 1, 2, 3 and 4. Figs. 1 and 2 are for sunrise, while figs. 3 and 4 are for sunset. From these curves we can at once know the time of sunrise and sunset at any height on any day of the year.

At Allahabad [Lat. 25° 25′ 25″] observations of penetration frequency for the F-layers were taken continuously for twentyfour hours in the months of October, November and December 1936, once a week and curves were drawn between the penetration frequency and the Indian standard time. These observations have been reported elsewhere by Pant and Bajpai.[6] From the curves given in their paper the time of minimum ionisation can be easily found out. Corresponding to this time of minimum ionisation the height at which sun's rays were falling can be read off from the curves in figs. 1 and 3. These are shown in the first part of table I. Similar tables have been made from data taken by Gilliland[1] for Washington [Lat. 39° 2′ 0″ N] and by Appleton[1] and Naismith for Slough [Lat. 51° 29′ 30″ N]. These tables form part 2 and part 3 of table I.

Table I

Part	Place	Date	Time of ground sunrise	T_1 Time of first mini-ionisation	Sunrise at height corresponding to T_1 in kms.	T_2 Time of second mini-ionisation	Height of sunrise corresponding to T_2 in kms.	Whether minimum before or after sunrise at F-layer
1	Allahabad [25° 25′ 25′]	3-10-36 ...	0553	0400	690	...	..	Before
		18-10-36 ...	0559	0400	735	...	...	,,
		15-11-36 ...	0617	0430	580	...	...	,,
		21-11-36 ...	0621	0530	135	0030	56560	After
2	Washington [39° 2′ 0″]	May, 1933 ...	0448	0400	76	...	...	After
		June, 1933 ...	0433	0400	35	..	...	,,
		July, 1933 ...	0440	0400	45	...	...	,,
		August, 1933 ...	0511	0200	980	...	...	Before
		September, 1933	0540	0430	175	...	...	After
		October, 1933...	0609	0430	358	2300	6030	Before
		November, 1933	0642	0600	58	2300	10500	After
		December, 1933	0711	0600	159	2300	7193	,,
		January, 1934...	0719	0600	208	2320	12310	,,
		February, 1934	0653	0510	403	2400	8740	Before
		March, 1934 ...	0613	0410	603	...	..	,,
		April, 1934 ...	0525	0400	246	...	...	,,
3	Slough [51° 29′ 30″]	15-1-34 ...	0800	0726	24	...	...	After
		15-2-34 ...	0717	0615	98	...	...	,,
		15-3-34 ...	0617	0526	69	...	...	,,
		15-4-34 ...	0507	0430	9	...	...	,,
		15-5-34 ...	0410	0335	23	...	...	,,
		15-6-34 ...	0342	0316	11	...	...	,,
		15-7-34 ...	0405	0340	7	...	...	,,
		15-8-34 ...	0445	0400	38	...	...	,,
		15-9-34 ...	0532	0455	42	...	...	,,
		15-10-34 ...	0630	0535	97	...	...	,,
		15-11-34 ...	0717	0615	88	...	.	,,

In table I the places for which the calculations have been made are shown in the second column. The dates for which calculations have been made are shown in column third. The time of ground sunrise is shown in column fourth. The time of first minimum ionisation just before sunrise is shown in column fifth. The height at which the sun rises at the time shown in column fifth is shown in column sixth. The time of second minimum ionisation before sunrise is shown in column seventh and the height at which the sun rises at the time given in column seventh, is shown in column eighth, while the ninth column shows whether the ionisation begins to rise before or after the sun rise in the F_2-region.

In the case of Allahabad and Slough the data are for particular day while for Washington they are the average of the whole month.

The data for Allahabad show that on 3rd October, 18th October, and 15th November, 1936, the ionisation begins to rise before sunrise at the F-region, while on the 21st November, 1936 it begins after the sunrise at the F-region. There is also a second minimum at 0030 on the same day. For Washington we see that in May, June, July, September, November and December, 1933 as well as in January 1934 the ionisation begins to rise after sunrise in the F-region, while in August and October, 1933 and February, March and April, 1934 it begins to rise before sunrise in the F-region. There is also a second minimum in October, November, December, January and February, always lying between 2300 and 2400. For Slough the ionisation begins to rise always after sunrise. However it is apparent from the data that in winter the height at which the sun is rising at the time of minimum ionisation is greater than in summer.

Conclusion

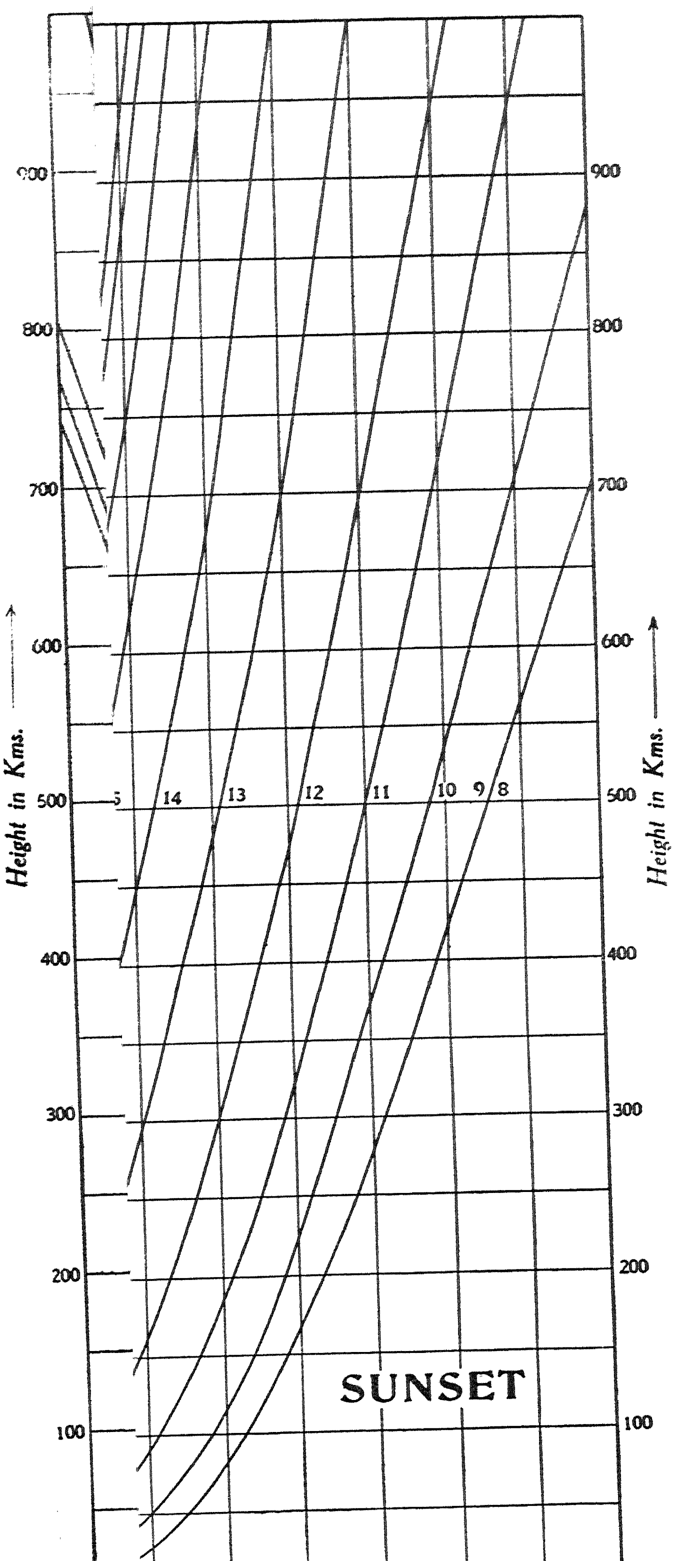
The data on the whole show that the height corresponding to the time of minimum ionisation is greater for winter than for summer for all latitudes. It also indicates that for higher latitudes, the ionisation in the F_2-region always begins to increase after the sun has risen in the regions from which the F_2-echoes are coming. This is evident from the data for Slough. For lower latitudes this is not so. For both Washington and Allahabad we find that at times the ionisation begins to increase before sunrise in the F_2-region, while at times the ionisation begins to increase after sunrise.

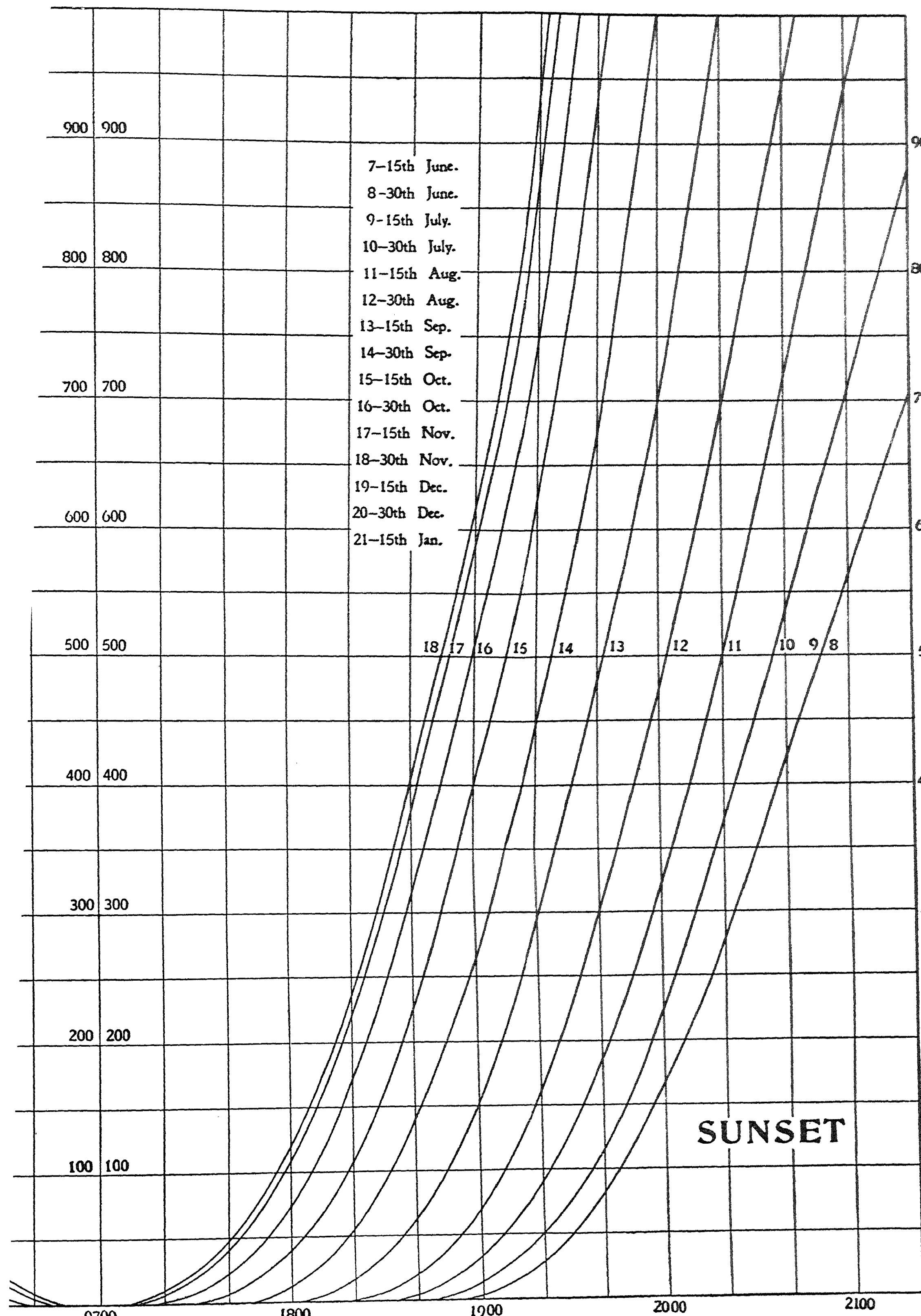
For lower latitudes we can roughly say that the ionisation begins to increase after sunrise in the F_2-region in summer and before sunrise in the F_2-region in winter.

My best thanks are due to Prof. M. N. Saha, Dr. G. R. Toshniwal and Mr. R. N. Rai for their keen interest and useful suggestions.

References

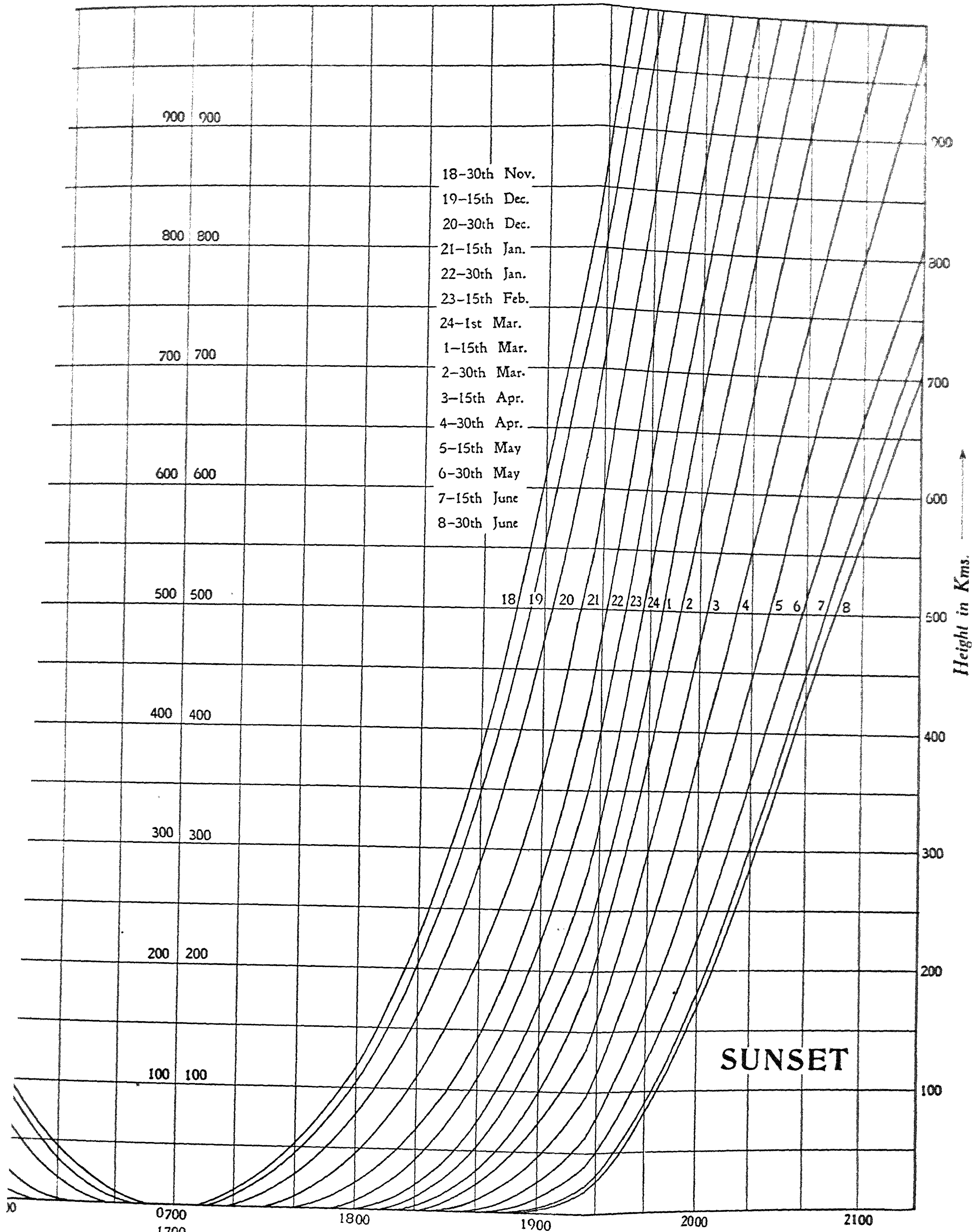
1. Appleton and Naismith (1935), *Proc. Roy. Soc. A*, **150**, 685.
2. Berkner and Wells (1934), *Terr. Mag.*, **39**, 215.
3. Berkner, Wells and Seaton (1936), *Terr. Mag.*, **41**, 173.
4. Gilliland (1935), *Proc. I.R.E.*, **23**, 1076.
5. Kirby, Berkner and Stuart (1934), *Proc. I.R.E.*, **22**, 481.
6. Pant and Bajpai (*awaiting publication*).
7. Pederson, *The Propagation of Radio Waves.*


Height in Kms.
900
800
700
600
500
400
300
200
100
0
15
14
13
12
11
10
9
8
SUNSET
2000
2100



7–15th June.
8–30th June.
9–15th July.
10–30th July.
11–15th Aug.
12–30th Aug.
13–15th Sep.
14–30th Sep.
15–15th Oct.
16–30th Oct.
17–15th Nov.
18–30th Nov.
19–15th Dec.
20–30th Dec.
21–15th Jan.
18 17 16 15 14 13 12 11 10 9 8
900 800 700 600 500 400 300 200 100
0700 1800 1900 2000 2100
Height in Kms.
SUNSET

Fig. 3



18–30th Nov.
19–15th Dec.
20–30th Dec.
21–15th Jan.
22–30th Jan.
23–15th Feb.
24–1st Mar.
1–15th Mar.
2–30th Mar.
3–15th Apr.
4–30th Apr.
5–15th May
6–30th May
7–15th June
8–30th June
SUNSET
Height in Kms.
0700
1700
1800
1900
2000
2100

Fig. 4